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A More Sophisticated Treatment of Collisions

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I. FRACTION OF MOLECULES CAPABLE OF COLLIDING

For A-type molecules, we have the fraction of molecules whose velocity components are between v_x and $v_x + dv_x$, etc., as

$$\frac{dN_A}{N_A} = \left(\frac{m_A}{2\pi kT}\right)^{\frac{3}{2}} e^{-m_A(v_x^2+v_y^2+v_z^2)/(2kT)} dv_x dv_y dv_z \tag{1.1}$$

and for B-type molecules, we have

$$\frac{dN_B}{N_B} = \left(\frac{m_B}{2\pi kT}\right)^{\frac{3}{2}} e^{-m_B(v_u^2+v_v^2+v_w^2)/(2kT)} dv_u dv_v dv_w \tag{1.2}$$

and the number of collisions between A-type and B-type molecules in these velocity ranges per unit time is:

$$dZ_{AB} = \frac{dN_A dN_B}{V^2} \pi d_{AB}^2 c_{AB} \tag{1.3}$$

where

$$c_{AB} = \sqrt{(v_x - v_u)^2 + (v_y - v_v)^2 + (v_z - v_w)^2}$$

Adding up all the collisions over all velocity ranges gives:

$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A}{V}\frac{N_B}{V}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2} \int dv_x \int dv_y \int dv_z \int dv_u \int dv_v \int dv_w$$
$$\left\{ e^{-m_A(v_x^2+v_y^2+v_z^2)/(2kT) - m_B(v_u^2+v_v^2+v_w^2)/(2kT)} \sqrt{(v_x - v_u)^2 + (v_y - v_v)^2 + (v_z - v_w)^2} \right\}$$

To proceed with the integration, it is convenient to convert to the center of mass coördinate system where

$$\dot{X}_{c.of.m.} = \frac{m_A v_x + m_B v_u}{m_A + m_B} = \delta$$

$$\dot{Y}_{c.of.m.} = \frac{m_A v_y + m_B v_v}{m_A + m_B} = \zeta$$

$$\dot{Z}_{c.of.m.} = \frac{m_A v_z + m_B v_w}{m_A + m_B} = \eta$$

and

$$\dot{x}_{AB} = v_x - v_u \equiv \alpha$$

$$\dot{y}_{AB} = v_y - v_v \equiv \beta$$

$$\dot{z}_{AB} = v_z - v_w \equiv \gamma$$

we can get the new differential volume element using the Jacobian (see Appendix), i.e.,

$$dv_x dv_y dv_z dv_u dv_v dv_w = J(\alpha,\delta)J(\beta,\zeta)J(\gamma,\eta) d\alpha d\beta d\gamma d\delta d\zeta d\eta$$

where each Jacobian looks like the first, i.e.,

$$J(\alpha,\delta) = \begin{vmatrix} \frac{\partial\alpha}{\partial v_x} & \frac{\partial\delta}{\partial v_x} \\ \frac{\partial\alpha}{\partial v_u} & \frac{\partial\delta}{\partial v_u} \end{vmatrix} = \begin{vmatrix} 1 & \frac{m_A}{m_A+m_B} \\ -1 & \frac{m_B}{m_A+m_B} \end{vmatrix} = 1$$

so

$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A}{V}\frac{N_B}{V}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2} \int d\alpha \int d\beta \int d\gamma \int d\delta \int d\zeta \int d\eta \; e^{-\mu(\alpha^2+\beta^2+\gamma^2)/(2kT) - (m_A+m_B)(\delta^2+\zeta^2+\eta^2)/(2kT)} \sqrt{\alpha^2+\beta^2+\gamma^2}$$

$$\int dZ_{AB} = \pi d_{AB}^2 \frac{N_A}{V}\frac{N_B}{V}\left(\frac{m_B}{2\pi kT}\right)^{3/2}\left(\frac{m_B}{2\pi kT}\right)^{3/2} \int d\alpha \int d\beta \int d\gamma \sqrt{\alpha^2+\beta^2+\gamma^2} e^{-\mu(\alpha^2+\beta^2+\gamma^2)/(2kT)} \int d\delta \int d\zeta \int d\eta e^{-(m_A+m_B)(\delta^2+\zeta^2+\eta^2)/(2kT)}$$

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where all integrals are over the range from $-\infty \to +\infty$.

We then have, since they are all standard integrals

$$\int dZ_{AB} = Z_{AB} = \pi d_{AB}^2 \frac{N_A}{V}\frac{N_B}{V}\left(\frac{m_A}{2\pi kT}\right)^{3/2}$$

$$\left(\frac{m_B}{2\pi kT}\right)^{3/2}\left(\left(\frac{2\pi kT}{m_A+m_B}\right)^{1/2}\right)^3 8\pi\left(\frac{kT}{\mu}\right)^2$$

and employing

$$\frac{1}{m_A}+\frac{1}{m_B}=\frac{1}{\mu}$$

one obtains (ρ is the number density!)

$$Z_{AB} = \pi d_{AB}^2 \rho_A\rho_B\left(\frac{\sqrt{\mu}}{2\pi kT}\right)^3 8\pi\left(\frac{kT}{\mu}\right)^2 \tag{1.4}$$

which is

$$Z_{AB} = \pi d_{AB}^2 \rho_A\rho_B\sqrt{\frac{8kT}{\pi\mu}} \tag{1.5}$$

For a pure A system, $\mu = m_A/2$ and $\rho_A = \rho_B = \rho$, and dividing by two to avoid the double count, one has

$$Z_{AA} = \frac{\pi d^2\rho\sqrt{2}}{2}\sqrt{\frac{8kT}{\pi m_A}} \tag{1.6}$$

II. MOLECULES COLLIDING WITH A WALL

The volume of the cylinder constructed in the figure is

$$cdt\cos\vartheta dS$$

and the number of molecules in that volume is

$$\rho cdt\cos\vartheta dS$$

where ρ is the number density. The fraction of those molecules which have the correct (appropriate) angle, and speed to actually strike the differential element of surface area on the wall, dS, in time dt is

$$\rho cdt\cos\vartheta dSKe^{-mc^2/(2kT)}c^2dc\sin\vartheta d\vartheta d\varphi$$

where K is the normalization constant.

$$dN = [\rho(c\cos\vartheta)]Ke^{-mc^2/(2kT)}c^2dc\times \sin\vartheta d\vartheta d\varphi(dSdt)$$

i.e.,

$$\int\frac{dN}{dSdt} = \rho K\int_0^{2\pi}d\varphi\int_0^{\pi/2}\cos\vartheta\sin\vartheta d\vartheta \; e^{-mc^2/(2kT)}c^3dc$$

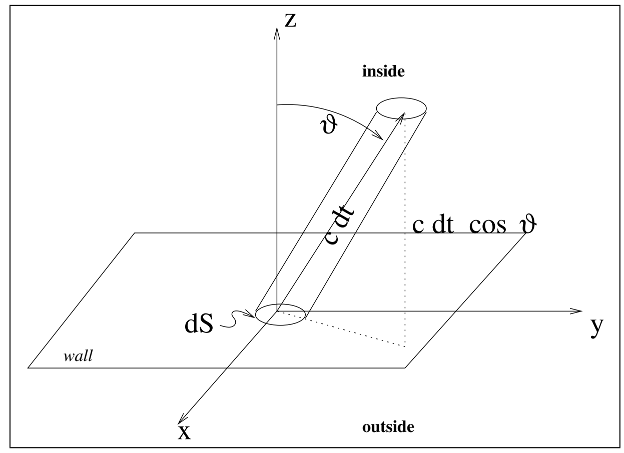

FIG. 1: Cylinder containing molecules which will collide with dS in time dt

Since

$$\int_0^{\pi/2}\cos\vartheta\sin\vartheta d\vartheta = -\left.\frac{\cos^2\vartheta}{2}\right|_0^{\pi/2} = \frac{1}{2}$$

and

$$\int_0^{2\pi}d\varphi = 2\pi$$

we have

$$\frac{dN}{dSdt} = \frac{1}{4\pi}\frac{1}{2}\bar{c}(2\pi) = \frac{\rho\bar{c}}{4}$$

III. APPENDIX

From elementary calculus, as example, the Jacobian connecting Cartesian to polar coördinates (in the plane) proceed from the definitions:

$$x = r\cos\varphi$$

and

$$y = r\sin\varphi$$

so

$$\frac{\partial(x,y)}{\partial(r,\varphi)} = J = \begin{vmatrix}\frac{\partial x}{\partial r} & \frac{\partial x}{\partial\varphi}\\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial\varphi}\end{vmatrix} = \begin{vmatrix}\cos\varphi & -r\sin\varphi\\ \sin\varphi & r\cos\varphi\end{vmatrix} = r$$

so $dxdy = rdrd\varphi$.